EFFECTS OF TEMPERATURE ON VAPOR LIQUID EQUILIBRIUM OF MTBE-METHANOL MIXTURES

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ABSTRACT

In separation process of binary mixture the vapor liquid equilibrium diagram is integral to design the separation apparatus. This research objective is to construct the vapor liquid equilibrium diagram for MTBE-Methanol binary mixture system at various temperatures and at constant pressure. Other objective is also to find the Azeotropic point which the MTBE-Methanol binary mixture formed at certain point that posed problems in separation processes. The separation process encountered problems during the Azeotropic point which vapor and liquid fraction is equal. The equipment used is Vapor Liquid Equilibrium Unit Equipment in the Unit Operation Laboratory. Initially the steps taken are to find the calibration curve for MTBE-Methanol mixture. The experiment started with MTBE volume set at constant and gradually increase the Methanol volume. The mixture in the equipment will be heated at four different temperatures which will give enough data to construct the diagram. Record the RI index and the temperature. The experiment was conducted at four different temperatures. The result, MTBE fraction of x vapor fraction and y liquid fraction formed Azeotropic point at 0.6~0.7 $= x = y$.

ABSTRAK

Dalam proses penapisan bahan kimia diagram untuk Wap dan Cecair diagram amat penting untuk membantu jurutera mereka alat penapisan. MTBE dan Methanol ialah produk yang terhasil daripada reaksi kimia Isobutylene. MTBE ialah bahan kimia yang digunakan sebagai bahan penambah yang boleh membantu pembakaran didalam minak Petrol. Salah satu masalah yang dihadapi dalam pemisahan antara MTBE dan Methanol ialah fenomena Azeotrope. Fenomena ini menyebabkan pecahan wap dan pecahan cecair mempunyai suhu didih yang sama. Pemisahan yang sedia ada adalah pemisahan yang memanipulasi suhu. Jika pecahan cecair dan pecahan wap mempunyai suhu didih yang sama, alat pemisahan tersebut tidak dapat memanipulasi suhu untuk memisahkan MTBE dan Methanol. Campuran binary ini mempunyai titik Azetrope pada 0.7 . Prosedure eksperimen ialah dengan melakukan ekperimen yang memvariasikan komposisi Methanol dan menetapkan isipadu MTBE didalam alat. Alat yang digunakan dalam eksperiman in ialah Vapor Liquid Equilibrium Unit yang terdapat di Makmal Unit Operasi.Konklusi yang boleh dibuat berdasarkan kajian ini ialah campuran binary MTBE-Methanol mampu menghasilkan titik Azeotrope dan Polyethylene Glycol tidak mampu memecahkan titik Azeotrope.

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NOMENCLATURE

y	-	Vapor fraction
x	-	Liquid fraction
P	-	Total Pressure
P_a	-	Partial pressure A
P_b		Partial pressure B
α_{AB}	-	Volatility A-B
$C_5H_{12}O$	-	*tert*-Butyl Methyl Ether
$wt\%$	-	Weight percent
x_b	-	Liquid Mole fraction B
x_a	-	Liquid Mole fraction A
y_a	-	Vapor mole fraction A
y_b	-	Vapor mole fraction B
cc	-	Cubic centimeter cm^3
CH_4O	-	Methanol

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The separation process depends heavily on both chemical and physical properties of the material needed to be separated. These properties determined the type of separation process. Separation process in the bigger picture used to transform a mixture of substances into two or more distinct product. Because the fundamental part of separation process is manipulating both chemical and physical properties of the elements aimed to be separated and the separated product could differ in chemical properties or physical properties such as size, boiling point and other properties. Bearing in minds almost every element or compound is found to be naturally in an impure state such as mixture of two or more components. Separation applications in the fields of chemical engineering are very important.

Separation processes can be essentially be defined as mass transfer, mass transfer occurs in distillation, absorption, drying, liquid-liquid extraction, adsorption, ion-exchange, crystallization, and membrane processes (Geankoplis, 2003) .Mass transfer is important in many areas of science and engineering it occurred when a component in mixture migrates in the same phase or from phase to phase because of difference in certain properties such as boiling point, concentration or component size this justify why separation process manipulate either chemical or physical properties as mentioned above (Geankoplis, 2003)The classification can be based on the mean of separation, mechanical or chemical. The choice of separation depends on

the pros and cons of each. Mechanical separations are usually favoured if possible due to the lower cost of the operations as compared to chemical separations. Systems that cannot be separated by purely mechanical means (e.g. crude oil), chemical separation is the remaining solution. The mixture at hand could exist as a combination of any two or more states: solid-solid, solid-liquid, solid-gas, liquid-liquid, liquid-gas, gas-gas, solid-liquid-gas mixture, etc.

Distillation is a unit operation or a physical separation process and not a chemical reaction. Commercially distillation has a number of applications. It used to separate crude oil into more fractions, other example is the distillation process used to distillate water to remove its impurities. Distillation process can be divided into two main types of distillation which is batch distillation and continuous distillation. Batch distillation refers to the use of distillation in batches, meaning that a mixture is distilled to separate it into its component fractions before the distillation still is again charged with more mixture and the process is repeated. This is in contrast with continuous distillation where the feedstock is added and the distillate drawn off without interruption. Batch distillation has always been an important part of the production of seasonal or low capacity and high-purity chemicals. It is a very frequent separation process in the pharmaceutical industry and in wastewater treatment units. And continuous distillation is an ongoing separation in which a mixture is continuously (without interruption) fed into the process and separated fractions are removed continuously as output streams as time passes during the operation (Juntao Zhanga, 2010).

The distillation process operated by manipulating the physical properties based on the volatility of the component in the mixture, the boiling point differences of the components in the mixture, using the boiling point is a way to separate the components from mixture is through heating process, by heating the mixture it will evaporate the components that have lower boiling point in comparison with the other components. This will leave behind the component that have higher boiling point that is still in liquid form. And to recover the evaporated components the condenser will be used condense the vapour back into liquid form. This is roughly the basic ideas behind distillation process. In much more complex system of distillation column the

vapour liquid equilibrium principles were used as guidelines in the distillation process. In industrial level each of the binary or ternary mixture contains a set vapour liquid equilibrium data that helps engineer to perform separation process. Vapour Liquid Equilibrium data are the reason this study is conducted.

The applications of distillations can be roughly divided in few groups, laboratory scale, and industrial distillation. The main difference between laboratory scale distillation and industrial is that laboratory scale is often performed batch-wise, whereas industrial distillation often occurs continuously.

However azeotropic phenomena limit the separation achievable by ordinary distillation. Complete separation of azeotropic mixtures requires either the coupling the distillation columns with other separation methods such as adsorption, membranes, and extraction or the use of more complex distillation schemes based on a modification of the equilibrium to effect the complete separation. Although many new separation techniques are being developed, distillation will remain the method of choice for large-scale separation of nonideal mixtures including azeotropic mixtures. Separation of such mixtures is achieved by use of one of the enhanced distillation methods. These include extractive distillation, salt distillation, pressure-swing distillation, reactive distillation, and azeotropic distillation. The latter method involves the use of entrainers to alter the relative volatility of the components and break the azeotrope. The choice of separation method depends on the specific system and economics (Silva, 2006).

1.2 Problem Statement

Binary mixture of MTBE-Methanol have been subject of numerous investigations in recent years because of their anti knock properties. However azeotropic phenomena limit the separation of this mixture achievable by ordinary distillation. Complete separation of azeotropic mixtures requires either the coupling the distillation columns with other separation methods such as adsorption, membranes, and extraction or the use of more complex distillation schemes based on a modification of the equilibrium to effect the complete separation. Although many new separation techniques are being developed, distillation will remain the method of choice for large-scale separation of nonideal mixtures including azeotropic mixtures. Separation of such mixtures is achieved by use of one of the enhanced distillation methods. These include extractive distillation, salt distillation, pressure-swing distillation, reactive distillation, and azeotropic distillation. The latter method involves the use of entrainers to alter the relative volatility of the components and break the azeotrope. The choice of separation method depends on the specific system and economics (Silva, 2006).

The final steps in the synthesis process of MTBE are the separations of the compound from the methanol via azeotropic distillations. The study of Vapour Liquid of the mixture is of great interest to supplement the design of the distillation processes, because the mixture showed deviations from Raoult`s Law that is positive azeotropic (Coto, 1997), positive or negative azeotrope will influence separations in terms of its efficiencies. Initial step in studying azeotropes is study on Vapour Liquid Equilibrium Diagram.

1.3 Objective

The objective of study is to investigate the effect of different temperature on Vapour Liquid Equilibrium of MTBE-Methanol binary mixture at constant atmospheric pressure 1atm.

1.4 Scope of Study

I. To obtain Vapour Liquid Equilibrium diagram for MTBE-Methanol binary mixture at various temperature at constant pressure.
II. To construct *x-y* and *T-xy* diagram for MTBE-Methanol at different temperature.
III. Determine azeotropic point of MTBE-Methanol mixture.

1.5 Rationale and Significance

Azeotrope has limits the separation achievable by ordinary distillation. It is possible to shift or break the azeotropic point by applying entrainer in separation process. To research on what type of entrainer that would work in enhancing separation process, the research on the Vapour Liquid Equilibrium of the mixture must be completed first. The significant of study into the Vapour Liquid Equilibrium is that it can provide data such as temperature, pressure and vapour/liquid fraction compositions that can be simplified in a diagram that could help the study of finding the entrainer (Al-Amer, 2000).

CHAPTER 2

LITERATURE REVIEW

2.1 Distillation

Distillation is the oldest and the most universal process of chemical technology and other branches of industry incorporating separation mixtures. Distillation, which is the most widely, used separation technique in the chemical process industries, accounts for about 3% of the world energy consumption. Although mature and well optimized, distillation remains an energy-intensive operation (Juntao Zhang, 2010). Distillation has substantial advantages over the other processes applied in order to separate a mixture, such extraction, crystallization, semi permeable membranes etc. As a rule, it is the most cost effective process, so it may be used for mixtures with diverse properties. This process is based on the fact that the composition of the boiling liquid and that of the vapour over it differ. Thus, if the boiling temperature is low (e.g., air separation), it is necessary to use low temperature refrigerants and conduct the process at a higher pressure. If it is high (e.g., in separation of heavy oil fractions or metals), high temperature heat carries or fire preheating have to be used and the process is run under vacuum. If the composition of the boiling point of the liquid and that of vapour over it are quite close, there is substantial energy consumption, which results in high capital costs. It is impossible to conduct the distillation process in the case of azeotropic composition (Petlyuk, 2004).

2.2 Batch Distillation

Batch distillation has always been an important part of the production of seasonal or low capacity and high-purity chemicals. It is a very frequent separation process in the pharmaceutical industry and in wastewater treatment units. In differential distillation, liquid is first charged to a heated kettle .The liquid charge is boiled slowly and the vapour are withdrawn as rapidly as they form to a condenser, where the condensed vapour or also known as distillate is collected. The first portion of vapour condensed will be richest in more volatile component. Heating an ideal mixture of two volatile substances A and B with A having the higher volatility, or lower boiling point in a batch distillation setup such as in Figure 2.1 until the mixture is boiling results in a vapour above the liquid which contains a mixture of A and B. Due to the higher volatility of A it will form vapour quickly and will rise up the upper section of the container. The vapour A goes through the condenser and is removed from the system. This in turn means that the ratio of compounds in the remaining liquid is now different from the initial ratio (i.e. more enriched in B than the starting liquid).The result is that the ratio in the liquid mixture is changing, becoming richer in component B. This causes the boiling point of the mixture to rise. If the difference in vapour pressure between the two components A and B is large (generally expressed as the difference in boiling points), the mixture in the beginning of the distillation is highly enriched in component A, and when component A has distilled off, the boiling liquid is enriched in component B (Geankoplis, 2003).

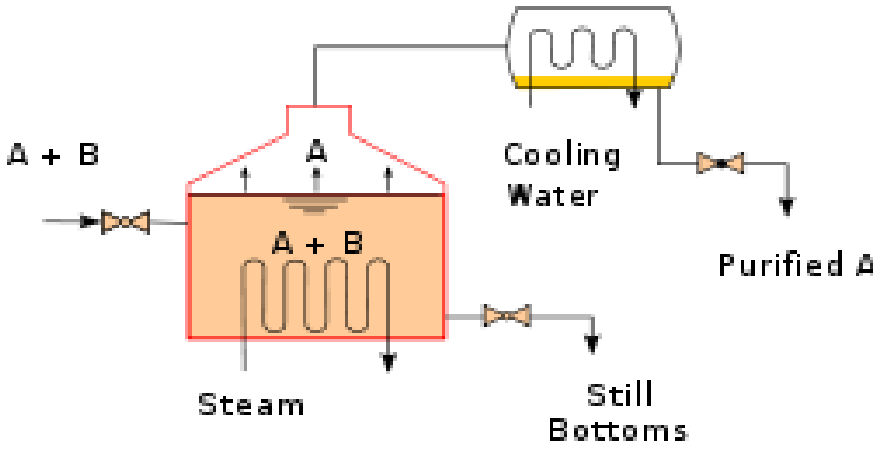

Figure 2.1: Batch Distillation

2.3 Continuous Distillation

Continuous distillation is an ongoing distillation in which a liquid mixture is continuously (without interruption) fed into the process and separated fractions are removed continuously as output streams as time passes during the operation. Continuous distillation produces at least two output fractions, including at least one volatile distillate fraction, which has boiled and been separately captured as a vapour condensed to a liquid. There is always a bottoms (or residue) fraction, which is the least volatile residue that has not been separately captured as a condensed vapour. Continuous distillation differs from batch distillation in the respect that concentrations should not change over time. Continuous distillation can be run at a steady state for an arbitrary amount of time. Given a feed of in a specified composition, the main variables that affect the purity of products in continuous distillation are the reflux ratio and the number of theoretical equilibrium stages (practically, the number of trays or the height of packing). Reflux is a flow from the condenser back to the column, which generates a recycle that allows a better separation with a given number of trays. Equilibrium stages are ideal steps where compositions achieve vapour-liquid equilibrium, repeating the separation process and allowing better separation given a reflux ratio. A column with a high reflux ratio may have fewer stages, but it refluxes a large amount of liquid, giving a wide column with a large holdup. Conversely, a column with a low reflux ratio must have a large number of stages, thus requiring a taller column. Continuous distillation requires building and configuring dedicated equipment. The resulting high investment cost restricts its use to the large scale. Figure 2.2 shows the process of continuous distillation (Geankoplis, 2003).

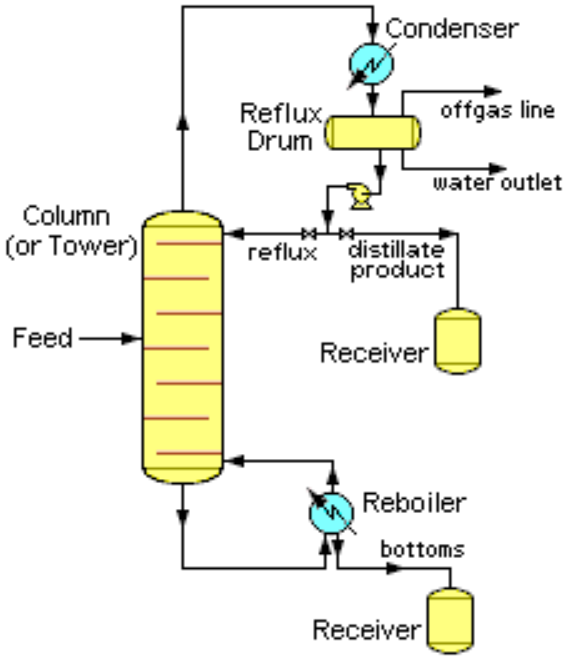

Figure 2.2: Continuous Distillation

2.4 Binary Mixture MTBE-Methanol

MTBE also known as methyl tertiary butyl ether and MTBE is a chemical compound with molecular formula $C_5H_{12}O$ .MTBE is a volatile, flammable and colourless liquid that is immiscible with water. MTBE has a minty odour vaguely reminiscent of diethyl ether, leading to unpleasant taste and odour in water. MTBE is a gasoline additive, used as oxygenate and to rise the octane number, although its use has declined in the United States in response to environmental and health concerns. The production of MTBE is from the chemical reaction of Isobutylene and Methanol but in this reaction not all the reactants turn to MTBE, Methanol still exist in the final product of this reaction which the Methanol is the undesired product so it is important to separate the undesired and the desired product.

2.4.1 Conventional production of MTBE

Methyl tertiary butyl ether is a high octane fuel additive and non-toxic as well as none polluting in contrast to lead alkyl additives. The high number of process licensors and plant under operation underline the economical importance of MTBE. The demand is predicted to increase from 8 to 32 million tons in the year 2000 making it worthwhile to improve existing production facilities. (Uwe Hommerich, 1998)

Figure 2.3 shows a schematic subdivision into three parts. In the reactor cascade, i-butene, which is available in C_4 −Raffinate from a steamcracking or catalytic cracking processes. Therefore, the effluent from the cascade consists mainly of MTBE, linear butenes (n-butenes) and excess methanol. Particularly the azeotrope formation of methanol with both MTBE and $-C_4$ poses difficulties on the subsequent product purification. In column 1 operated at 6 bar, the reactor effluent is separated into and n$-C_4$ /methanol distillate with azeotropic composition and a bottom product containing approximation of 97 wt% MTBE and 3 wt% methanol. The distillate is fed to third process part where high selectivity of the etherification is used for producing pure n-C_4 hydrocarbons. The MTBE /methanol stream of column 1 is fed to third process part where high selectivity of the etherification is used for producing pure n-C_4 hydrocarbons. The MTBE/methanol stream of column 1 is fed to a second distillation at 12 bars in order to achieve the final product quality of over 99 wt% for MTBE. The MTBE/methanol azeotrope at the top of column 2 has to be recycled into the reaction zone, since an economical separation is not feasible because of the small amount (approx. 4% of the reactor effluent) (Uwe Hommerich, 1998).

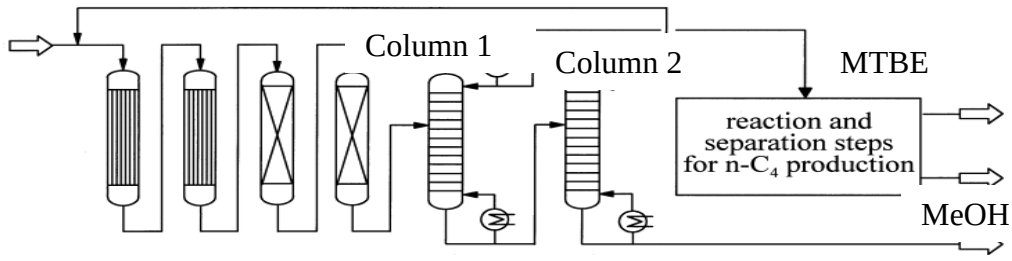

Figure 2.3: Production of MTBE schematic diagram (Uwe Hommerich, 1998)

2.5 Importance of Vapour-Liquid Equilibrium Diagram

VLE is a set of data necessary especially for engineer in separation process. This data is importance in chemical industries. Most industries handle two type of distillation which is continuous and batch distillation, and VLE is at the heart of the process as it provides guidance at how to design of the distillation equipments itself.VLE is especially important to continuous distillation or fractional distillation. In distillation it is importance to have a boiling diagram of the binary mixture. The diagram provide the information of the mixture in terms of which components is more volatile(boiling point) and which is less volatile(higher boiling point).In the boiling point diagram it also show the fraction of the mixture at different temperature and pressure. This information is paramount to conduct any distillation process. Once the data acquired this will provide the engineer at what temperature and at what pressure should the distillation process be proceeds and provide how much distillate will be resulted from distillation and how much condensate will be obtained. And this much more importance particularly for the continuous distillation process A mathematical and graphical method for determining the numbers of theoretical trays or stages in distillation column needed for a distillation process have been developed by McCabe Thiele method in 1925. McCabe-Thiele method is considered the simplest and perhaps most instructive method for analysis of binary distillation. This method uses the fact that the composition at each theoretical tray (or equilibrium stage) is completely determined by the mole fraction of one of the two components (Geankoplis, 2003).

2.6 Theory of Vapour Liquid Equilibrium

As in gas-liquid systems the equilibrium in vapour liquid system is restricted by the phase rule. For two components system and two phases there are four variables which are temperature, pressure and compositions of y_a which is the fraction mixture in vapour condition and x_a which is in liquid conditions. In the mixture of two components let say MTBE and Methanol the mixture is in two phase

vapour and liquid. .VLE is a set of data obtained experimentally to provide ways for engineer to separate the mixture effectively. VLE is a condition where a liquid and its vapour (gas phase) are in equilibrium with each other, a condition or state where the rate of evaporation (liquid changing to vapour) equals the rate of condensation (vapour changing to liquid) on a molecular level such that there is no net (overall) vapour-liquid interconversion. Although in theory equilibrium takes forever to reach, such an equilibrium is practically reached in a relatively closed location if a liquid and its vapour are allowed to stand in contact with each other long enough with no interference or only gradual interference from the outside. There are many types of VLE. VLE can be of one component and or more than one.VLE that comprise more than one component were called binary mixture (two components) of ternary for three components. It said that the more components we have in VLE the more complicated it will be (Geankoplis, 2003)

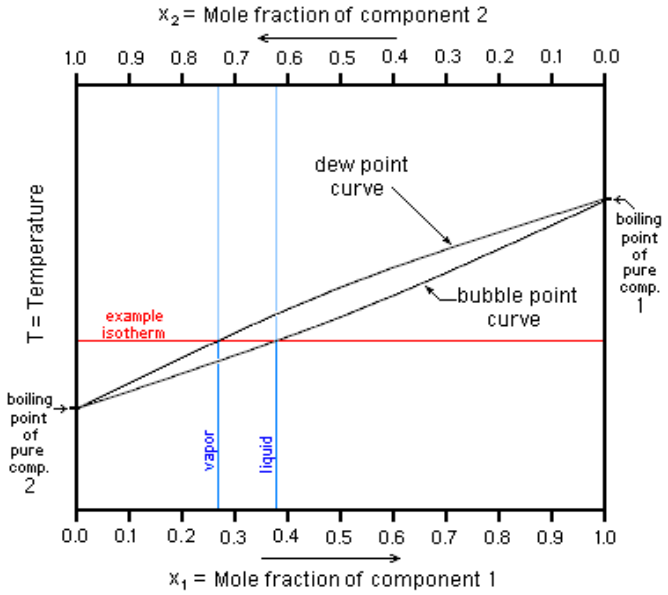

Figure 2.4: VLE Diagram of Binary Mixture

Figure 2.4 the binary mixture of two components. Often the VLE relations for a binary mixture let say A(MTBE) and B(Methanol) are given as a boiling point diagram as shown above. The upper line is the saturated vapour line (or the dew point line) and the lower line is the saturated liquid line (the bubble point line).The region between those lines is the area which vapour and liquid are in mixture. In other word the mixture is between those line is a two phase region. The

concentration of a vapour in contact with its liquid, especially at equilibrium, is often given in terms of vapour pressure, which could be a partial pressure (part of the total gas pressure) if any other gas are present with the vapour. The equilibrium vapour pressure of a liquid is usually very dependent on temperature. At vapour-liquid equilibrium, a liquid with individual components (compounds) in certain concentrations will have an equilibrium vapour in which the concentrations or partial pressures of the vapour components will have certain set values depending on all of the liquid component concentrations and the temperature. It also means that if a vapour with components at certain concentrations or partial pressures is in vapour-liquid equilibrium with its liquid, then the component concentrations in the liquid will be set dependent on the vapour concentrations, again also depending on the temperature. The equilibrium concentration of each component in the liquid phase is often different from its concentration (or vapour pressure) in the vapour phase, but there is a correlation. Such VLE concentration data is often known or can be determined experimentally for vapour-liquid mixtures with various components. In certain cases such VLE data can be determined or approximated with the help of certain theories such as Raoult's Law, Dalton's Law, and/or Henry's Law (Geankoplis, 2003).

2.6.1 Raoult`s Law

The law was established by by François-Marie Raoult`s. Raoult's law states the vapour pressure of an ideal solution is dependent on the vapour pressure of each chemical component and the mole fraction of the component present in the solution which in mathematical is expressed as:

$$P_a + P_b = P \quad \textbf{(2.1)}$$

$$x_a + x_b = 1 \quad \textbf{(2.2)}$$

$$P_a x_a + P_b x_b = P \quad \textbf{(2.3)}$$

P is the total pressure vapour pressure of all the components exist in the mixture consequently, as the number of components in solution increases, the

individual vapour pressures decrease, since the mole fraction of each component decreases with each additional component. If a pure solute which has zero vapour pressure (it will not evaporate) is dissolved in a solvent, the vapour pressure of the final solution will be lower than that of the pure solvent. This law is strictly valid only under the assumption that the chemical interactions between the two liquid is equal to the bonding within the liquids: the conditions of an ideal solution. The vapour pressure and composition in equilibrium with a solution can yield valuable information regarding the thermodynamic properties of the liquids involved. Raoult's law relates the vapour pressure of components to the composition of the solution. The law assumes ideal behaviour. It gives a simple picture of the situation just as the ideal gas law does. The ideal gas law is very useful as a limiting law. As the interactive forces between molecules and the volume of the molecules approaches zero, so the behaviour of gases approach the behaviour of the ideal gas (Geankoplis, 2003)

2.6.2 Relative Volatility

Relative volatility is a measure comparing the vapour pressures of the components in a liquid mixture of chemicals. This quantity is widely used in designing large industrial distillation processes. In effect, it indicates the ease or difficulty of using distillation to separate the more volatile components from the less volatile components in a mixture. By convention, relative volatility is usually denoted as α. Relative volatilities are used in the design of all types of distillation processes as well as other separation or absorption processes that involve the contacting of vapour and liquid phases in a series of equilibrium stages. In order to separate a binary mixture using distillation process, there must be differences in volatilities of the components. A numerical measure of this separation is the relativity α_{AB} .This is defined as the ratio of the concentration of A in the vapor to the concentration of A in the liquid divided by the ratio of the concentration of B in the vapour to the concentration of B in the liquid (Geankoplis, 2003)

$$\alpha_{AB} = \frac{Y_A/X_A}{Y_B/X_B} = \frac{Y_A/X_A}{1-Y_A/1-X_A} \quad \textbf{(2.4)}$$

Where α_{AB} is the relativity of volatility of A with respect to B in the binary system if the system obeys the Raoult`s Law as does the benzene- toluene system.

$$y_A = \frac{P_A x_A}{P} \qquad y_B = \frac{P_B x_B}{P} \tag{2.5}$$

$$\alpha_{AB} = \frac{P_A}{P_B} \tag{2.6}$$

2.7 Azeotrope

Departures of the Raoult`s Law frequently manifest themselves in the formation of azeotropes particularly mixtures of close boiling species of different chemical types whose liquid solutions are non ideal. azeotropes are formed by liquid mixtures exhibiting maximum and minimum boiling point. These represent, respectively negative or positive deviations from Raoult`s Law. Vapour and liquid compositions are identical at the azeotropic compositions thus all the K values are 1 and no separation can take place. There are types of azeotropes that are commonly encountered with the binary mixture. The most common type by far is the minimum boiling homogenous azeotrope. Heterogeneous azeotrope is always minimum boiling point mixture because activity coefficient must be significantly greater than 1 to cause the splitting into two liquid phases. This is true for the MTBE –Methanol mixture which showed minimum azeotrope position. azeotropes limit the separation achievable by ordinary distillation. It is possible to shift the equilibrium by changing the pressure sufficiently to break azeotrope or move it away from the region where required separation must take place (j.d. seaders, 1998)

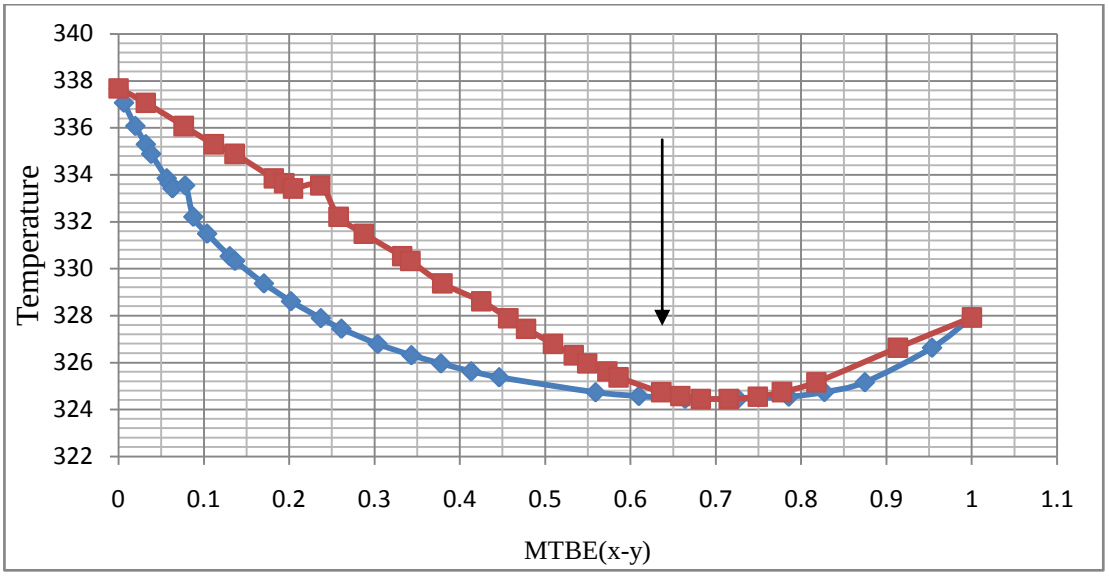

Figure 2.5: MTBE-Methanol VLE Diagram

The Figure 2.5 shows the T-*xy* diagram of MTBE-Methanol mixture. This is an example of minimum boiling point azeotrope. From figure it showed that MTBE-Methanol formed azeotropic point at 51 ℃ and at compositions of 0.7052 liquid(*x)* and also 0.7052 of vapour(*y)* (Gmehling, 2002). At this point the Azeotropic formed the minimum boiling point or positive azeotrope highlighting that this is the positive deviation of Raoult`s Law.

2.7.1 Azeotrope Distillation

Interactions between the components of the solution create properties unique to the solution, as most processes entail nonideal mixtures, where Raoult`s Law does not hold. Such interactions can result in a constant boiling azeotrope which behaves as if it were a pure component in the same proportion as the vapour, so the evaporation does not change the purity, and distillation does not affect separation. For example, ethyl alcohol and water form an azeotrope of 95.6% at 78. ℃ .

If the azeotrope is not considered sufficiently pure for use, there exist some techniques to break azeotrope to give pure distillate. This set of techniques is known as azeotropic distillation. Some techniques achieve this by jumping over the